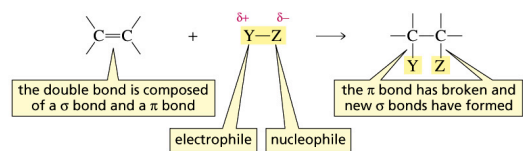


## Chapter 4

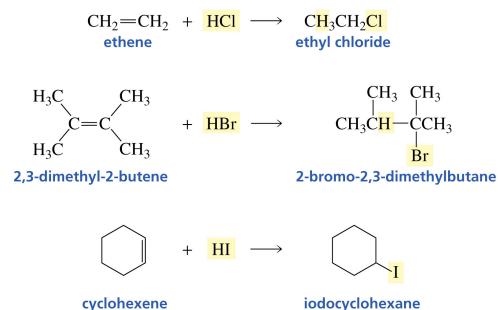
### Reactions of Alkenes

Adapted from Profs. Turro & Breslow, Columbia University and Prof. Irene Lee, Case Western Reserve University

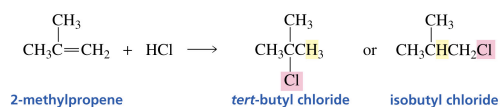
## Electrophilic Additions: Alkenes



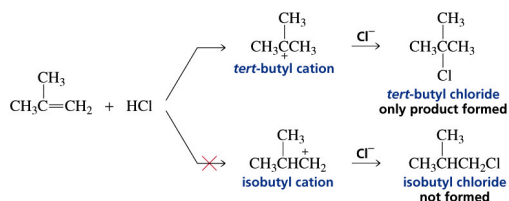
## Addition of Hydrogen Halides



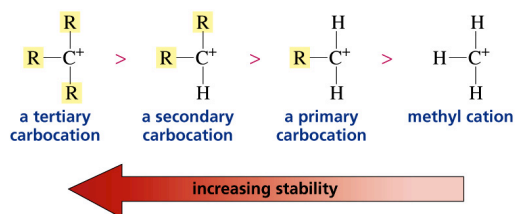
## What is the product?



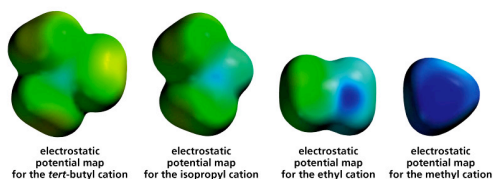
## Carbocation formation is the rate-limiting step



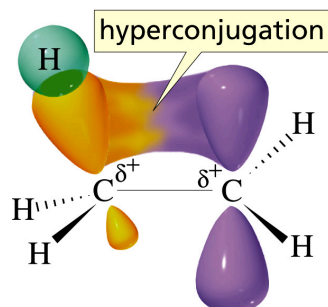
## Carbocation Stabilities



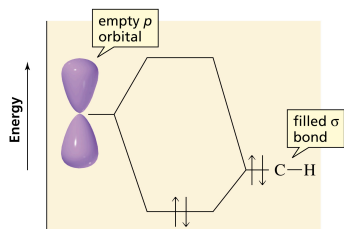
Alkyl groups decrease the concentration of positive charge in the carbocation



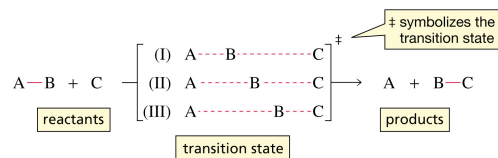
## Delocalization of Electrons



## Molecular Orbital Diagram in a Hyperconjugation System

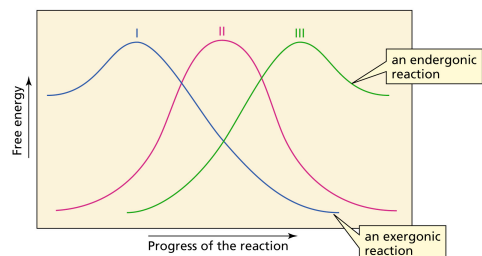


*Hammond postulate: the transition state will be more similar to the species that it is closer to energetically*



Exergonic reaction: early transition state resembles reactants (I).

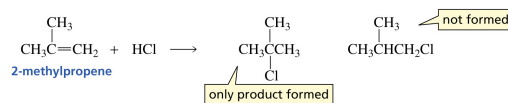
Endergonic reaction: late transition state resembles products (II).



I: early transition state (Like reactants)    II: mid-transition state    III: later transition state (Like products)

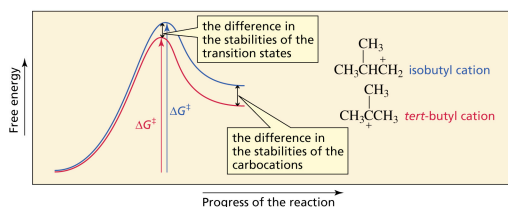
## Markovnikov's Rule

The electrophile adds to the  $sp^2$  carbon that is bonded to the greater number of hydrogens



In a regioselective reaction, one constitutional isomer is the major or the only product.

Explained by the intermediates, for example:  
*tert*-butyl cation is formed faster and it is more stable than isobutyl.

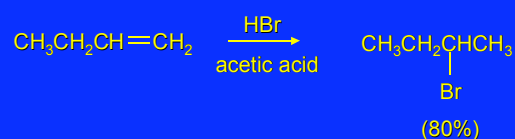


## Regioselectivity of Hydrogen Halide Addition: Markovnikov's Rule

### Markovnikov's Rule

When an unsymmetrically substituted alkene reacts with a hydrogen halide, the hydrogen adds to the carbon that has the greater number of hydrogen substituents, and the halogen adds to the carbon that has the fewer hydrogen substituents.

### Markovnikov's Rule



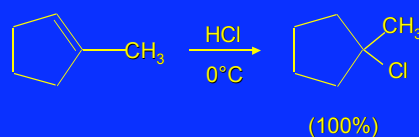
Example 1

### Markovnikov's Rule



Example 2

### Markovnikov's Rule

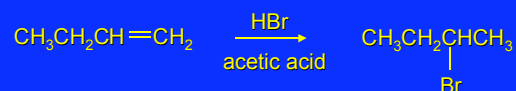


Example 3

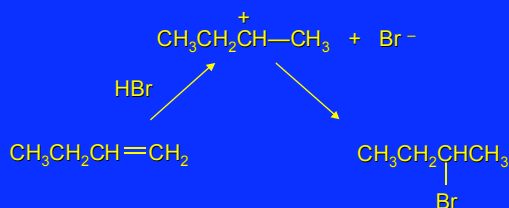
## Mechanistic Basis for Markovnikov's Rule

Protonation of double bond occurs in direction that gives more stable of two possible carbocations.

### Mechanistic Basis for Markovnikov's Rule: Example 1

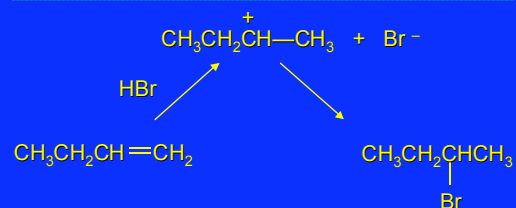


### Mechanistic Basis for Markovnikov's Rule: Example 1

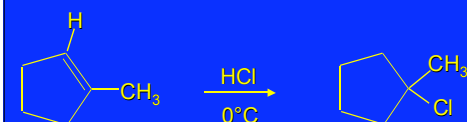


### Mechanistic Basis for Markovnikov's Rule: Example 1

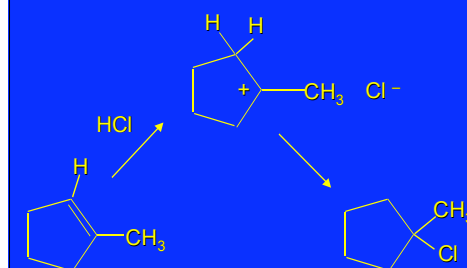
$\text{CH}_3\text{CH}_2\text{CH}_2-\overset{+}{\text{CH}}_2$   
primary carbocation is less stable: not formed

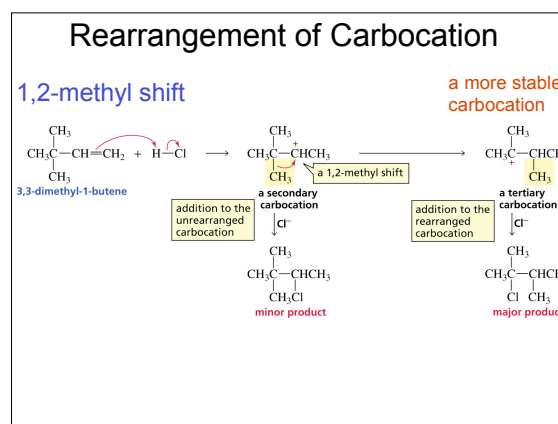
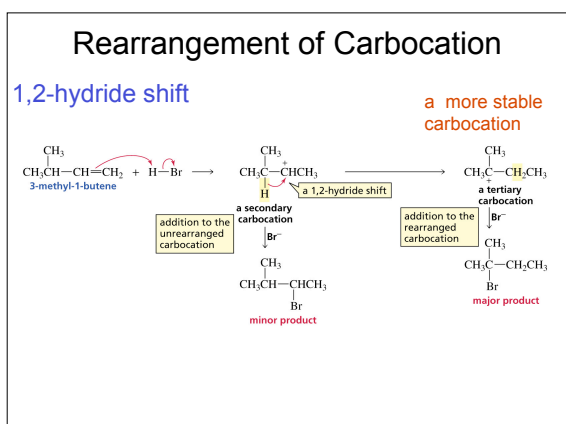
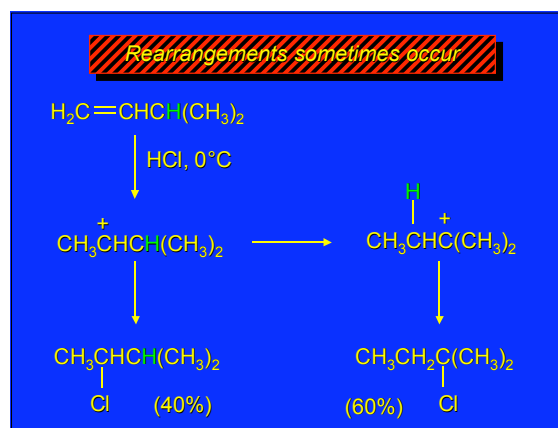
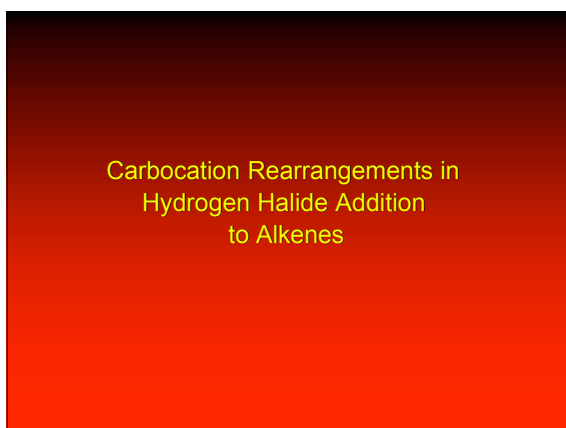
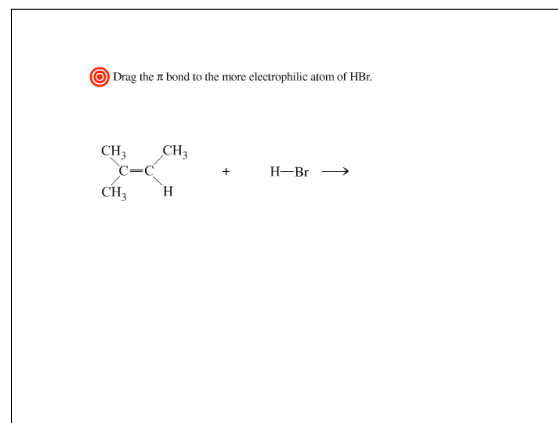
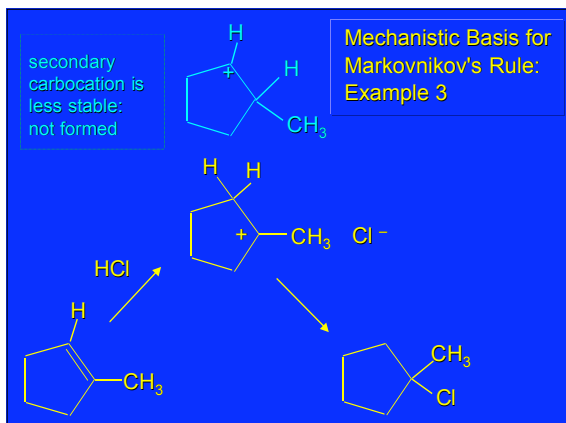


### Mechanistic Basis for Markovnikov's Rule: Example 3



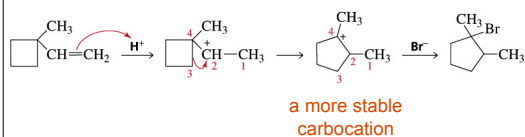
### Mechanistic Basis for Markovnikov's Rule: Example 3



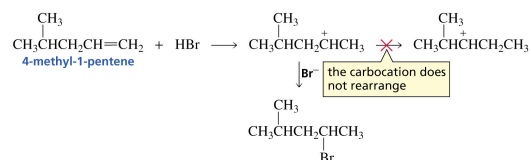


## Carbocation Rearrangement

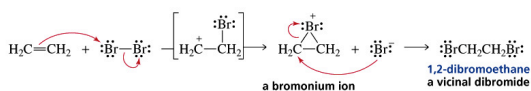
### Ring Expansion



### Carbocation does not always rearrange ...



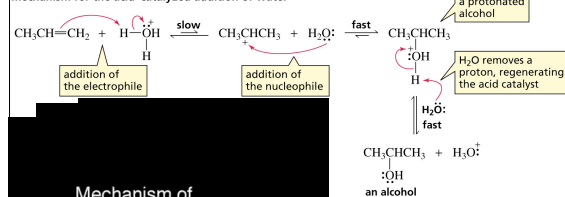
## Addition of Halogens to Alkene



The Halonium Ion 1

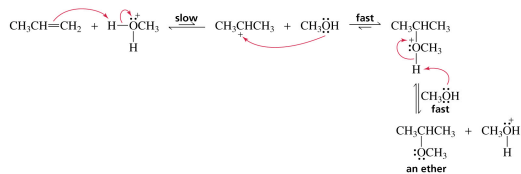
## Addition of Water to Alkene (alcohols)

mechanism for the acid-catalyzed addition of water



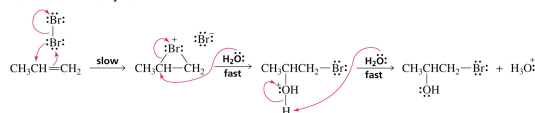
Mechanism of Hydration 1

## Acid-Catalyzed Addition of Alcohol (ethers)



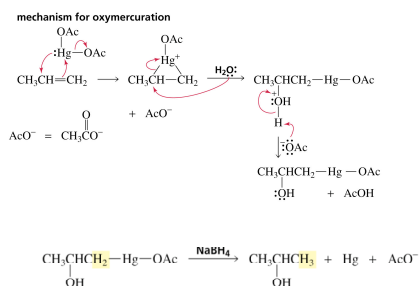
## Addition of Halogens in the Presence of Water (halohydrins)

mechanism for halohydrin formation



## Oxymercuration and Mercuration of Alkene

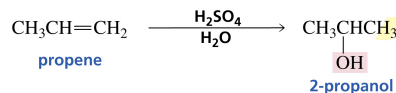
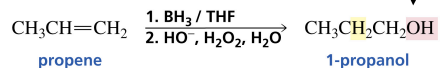
(alcohols w/o carbocation rearrangement)



## Addition of Borane

### Hydroboration–Oxidation

Anti-Markovnikov's rule in product formation  
(less substituted alcohols)

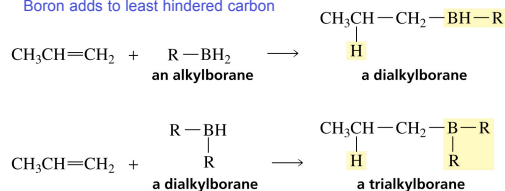


Vs. Markovnikov's rule in product formation  
(more substituted alcohols)

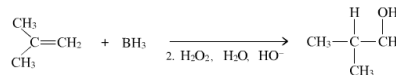
## Formation of Alkyl Boranes

Anti-Markovnikov  
Addition

Boron adds to least hindered carbon



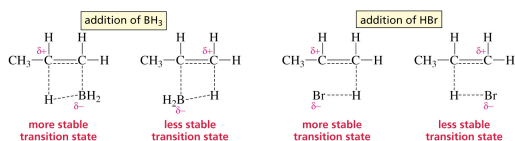
Hydroboration–oxidation adds the elements of water to an alkene. In the first step, borane adds from one side of the alkene. Click "Begin" to start.



Begin

Anti-Markovnikov  
Addition

Boron adds to least hindered carbon and is replaced w/ -OH by oxidation

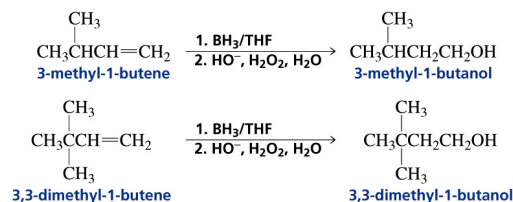


(A type of pericyclic reaction; important reaction and mechanism in directing reactions both regio- and stereo-selectively.)

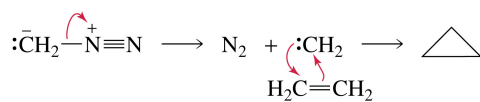
Markovnikov  
Addition

Formation of the most stable carbocation

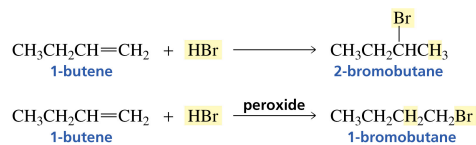
## Examples of Anti-Markovnikov Addition of an OH Group



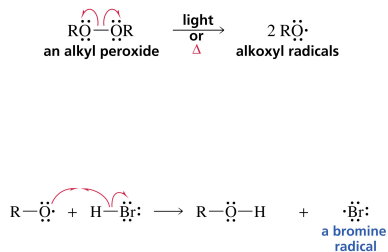
## Carbene: another reactive intermediate Reaction with an Alkene



## Synthesis of Bromobutane Isomers

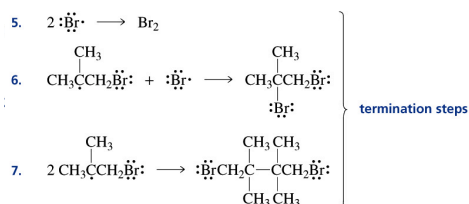


## Generation of Free Radicals Using 1/2 arrows for the movement of one electron

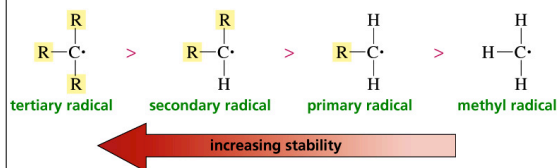


## Addition of Radicals to Alkenes

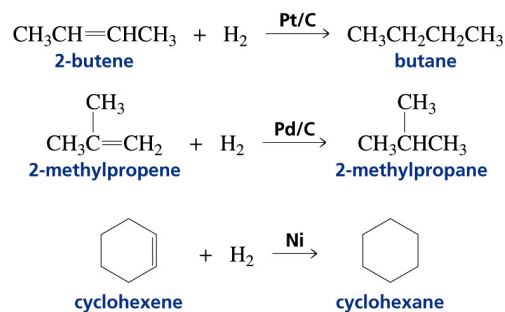
Initiation → Propagation → Termination



## Relative Stabilities of Alkyl Radicals



## Addition of Hydrogen to Alkenes





## Catalytic Hydrogenation of an Alkene

